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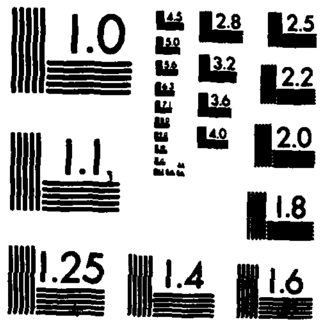

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SUMMARY REPORT

POLYCYCLIC HIGH ENERGY OXIDIZERS

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Prepared for: The Office of Naval Research
Dr. R. Miller/Contract Monitor

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APRIL 1983

Morton Thiokol/Wasatch Division
P. O. Box 524
Brigham City, UT 84302

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POLYCYCLIC HIGH ENERGY OXIDIZERS

by

J. C. Hinshaw

A report on work sponsored by the
Office of Naval Research

Contract N0014-81-C-0204

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Nitramines
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tris(acylamino)methanes

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Efforts toward the synthesis of polycyclic high density, high energy oxidizers have involved examination of synthetic paths to the hexaazaadamantane framework. Routes examined include condensation of amides with an orthoformate, reaction of tris(acylamino) methanes with orthoformate and cyclizations based on acylated perhydrotriazines. The cyclization chemistry of a pentaazabicyclononadiene is also under investigation.

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20. Abstract (continued)

Several routes to tetranitrazabicyclooctane ("bicyclic HMX") have also been examined including modification of the preformed tetraazabicyclooctane ring system and cyclization approaches.

CONTENTS

INTRODUCTION

The object of this program has been to synthesize and evaluate new high density, high energy, polycyclic nitramine/nitro containing oxidizers for solid propellant/explosive applications.

TECHNICAL DISCUSSION

A direct approach to the development of new high energy propellants with improved ballistic characteristics involves the design, synthesis, and development of new high energy oxidizers as HMX/RDX replacements. The ideal HMX/RDX alternative would incorporate many physical properties superior to HMX/RDX in addition to providing propellant compositions with much improved ballistic flexibility.

Approach

In considering compounds for potential use as new high energy oxidizers, we have selected organic compounds having a minimum of hydrogen (favors less water formation in propellant combustion products for minimum signature exhaust applications) and high $-NO_2$ functionality (favors high energy with a minimum loss in thermal stability). In addition, we propose to incorporate these features into symmetrical polycyclic structures resulting in the advantages outlined below:

1. Increased Density. The general increase in density observed in progressing from acyclic through monocyclic to polycyclic organic structures is well known (e.g., graphite $\sim$2.1 g/cm^3, diamond = 3.5 g/cm^3; decane = 0.73 g/cm^3, cyclodecane = 0.89 g/cm^3, adamantane = 1.07 g/cm^3). Application of this general trend from HMX (1.9 g/cm^3 to the polycyclic target molecules shown below leads to predicted densities of $\geq$2 g/cm^3 for

these compounds. Furthermore, calculation of estimated densities from empirical atomic volumes[1] also leads to values of ≥ 2 g/cm^3 for the target compounds proposed.

2. Increased Energy. All the proposed target molecules possess oxygen balance and estimated[2] heats of formation superior to those of HMX.

3. Improved Stability. It has long been recognized that many polycyclic structures, such as the adamantane cage system, impart increased thermal stability to the hydrocarbon molecule.[4] This polycyclic approach to improved high energy oxidizers, as exemplified by the proposed target molecules, had not heretofore been examined. Furthermore, the proposed nitramine/nitro functionalities are not expected to result in unfavorable chemical or hydrolytic instability.

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1. D. A. Cichra, J. Holden, and C. Dickenson Estimation of "Normal" Densities of Explosive Compounds from Empirical Atomic Volumes, Naval Surface Weapons Center Report, NSWC TR-79-273, February 19,1980.

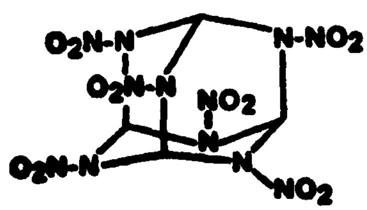
2. Estimated heats of formation are calculated using a method developed[3] by A. D. Little, Inc., and extended by Thiokol/Wasatch. However, a lack of information on oxidizing functionality incorporated in polycyclic ring systems renders calculations on these types of structures difficult and of unknown reliability at this time.

3. "Calculation of Heats of Combustion of Organic Compounds from Structural Features," A. D. Little, Inc., Report, Contract DH19-020-ORD-47, May 1952.

4. R. C. Fort, Jr., "Adamantane, the Chemistry of Diamond Molecules," Studies in Organic Chemistry Series, Vol. 5, P. G. Gassman, Ed, Marcel Deckler, Inc., New York, 1976.

4. Ballistic Tailorability. The cause(s) involved in the problem of ballistic inflexibility of HMX-RDX oxidized propellant systems is being investigated.[5] The synthesis of the new high energy nitramine oxidizers proposed here will make available new materials for ballistic studies which are important for a general understanding of structure vs. combustion phenomenon.

Examples of some target compounds are shown below:



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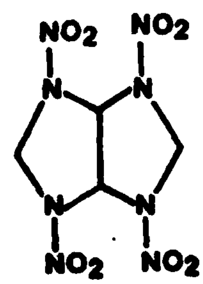

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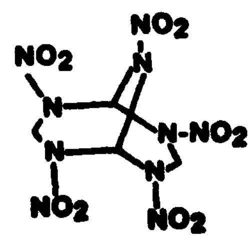


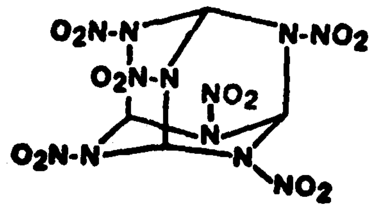
III

5. K. P. McCarty in 14th JANNAF Combustion Meeting, CPIA Publication 292, Vol. 1 p. 243, U. S. Air Force Academy, August 1977.

Little is known regarding the synthesis of such polyaza, polycyclic molecules. Work has, therefore, been directed toward the development of new chemical methods for the construction of such systems. Recent work has focused on the study of the addition of polyfunctional nitrogen nucleophiles to electron deficient nitrogen hetrocycles as new unexplored routes to these compound types.

Synthesis

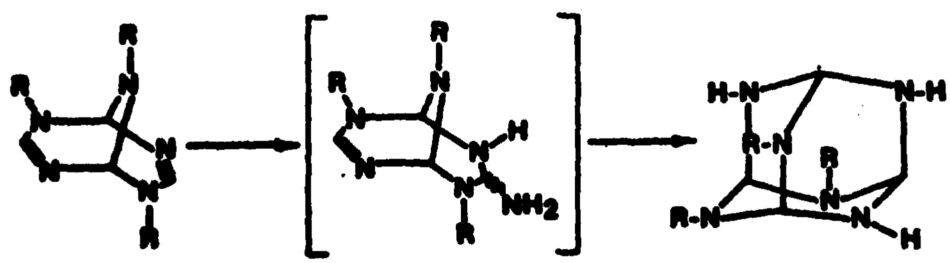
Compound I, N^1, N^2, N^3, N^4, N^5, N^6 - hexanitro - 2, 4, 6, 8. 9. 10 - hexaazaadamantane.



The hexaazaadamantane ring system remains unknown. We have scrutinized several viable synthetic routes to the cage structure.

Earlier we examined a new cyclization approach to hexaazaadamantane from the supposedly known [6] pentaazabicyclo[3.3.1]nonadiene 1.

Scheme I



1 2 3

6. Netherlands Patent, 6,500, 521; see Chem Abstracts, 64 2116a (1966).

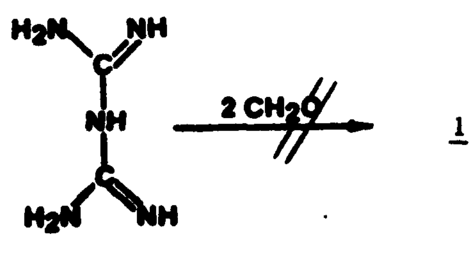
Thus, addition of ammonia to one amidine linkage in 1 was expected to lead to 3 via cyclization of 2. Similar synthetic schemes have been used to prepare heteroadamantanes 5 starting from the carbocycle 4[4] (see Scheme II).

Scheme II

4 5

Attempts to carry out the reaction sequence of Scheme I were frustrated when it was found that the reported preparation of 1 was in error. In our hands, repeated attempts to prepare 1 using the reaction of cyanoguanidine and ammonium chloride with formaldehyde led only to polymeric materials with no usable amounts of the bicyclic product being detected.

Attention was then turned toward alternate routes for the preparation of the desired pentaazabicyclononadine 1. Reaction of biguanide 6 with formaldehyde gave only polymeric material and not the desired 1.



6

In another approach the n-benzyldihydrotriazine[7] 7 was prepared and its reaction with formaldehyde examined.

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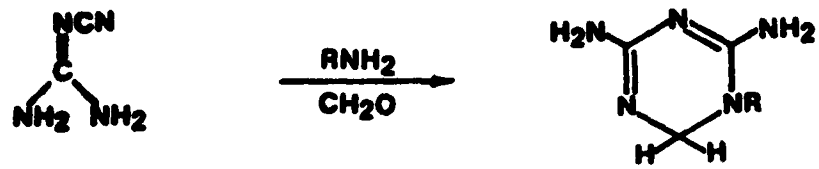
7. See: W. D. Spietoff, Z. Chem. 7, 342 (1967).



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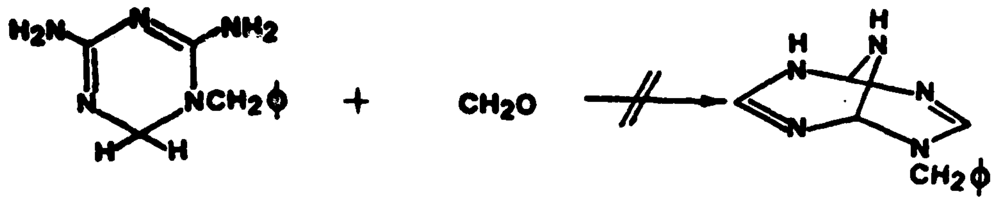
However, under all conditions examined, no evidence has been obtained for the formation of the desired N-benzylpentaazabicyclononadiene 8.



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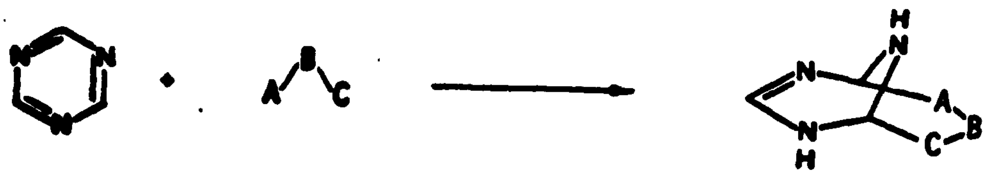
Attention was then turned to the reaction of s-triazine 9 with bifunctional reagents as a potential new route to the pentaazabicyclo[3.3.1]nonane system.



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Nucleophilic reagents are known to add to electron deficient nigrogen hetrocycles such as 9.[8] The reaction of 1,3-ambident nucleophiles with such systems may involve bicyclic intermediates[9] which have been isolated in some instances.[10]

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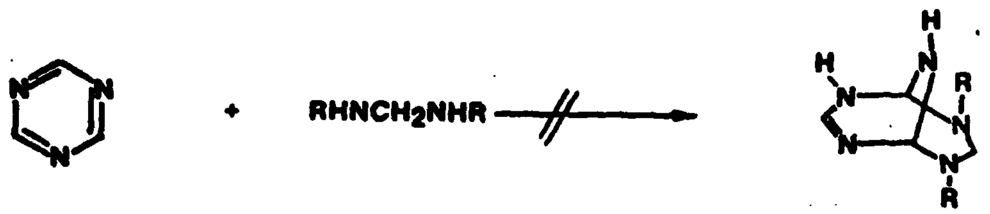
8. H. C. Van der Plas, "Ring Transformations of Heterocycles," Academic Press, New York, 1973, Vol. 2.

9. P. Barczynski and H. C. Van der Plas, J. Org. Chem., 47, 1077 (1982).

10. J. J. Fox, T-L. Su, L. Stempel, and K. Watanable, J. Org. Chem, 47, 1081 (1982).

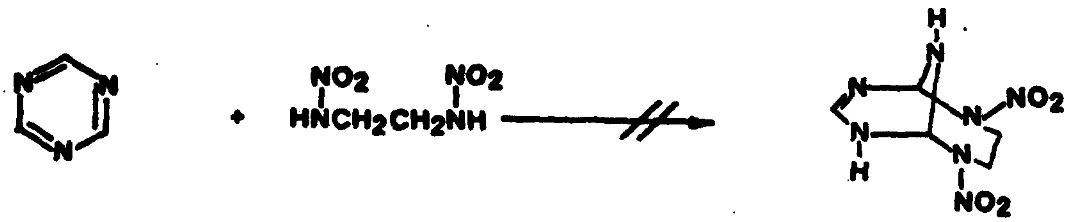
Particularly intriguing was the possible cyclization of methylenedinitramine with 9 leading to 10, a direct precursor of the target oxidizer II.



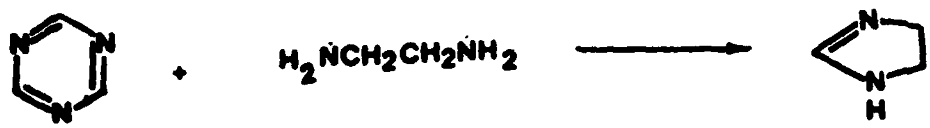
R = $-NO_2$, $-COCH_3$

10

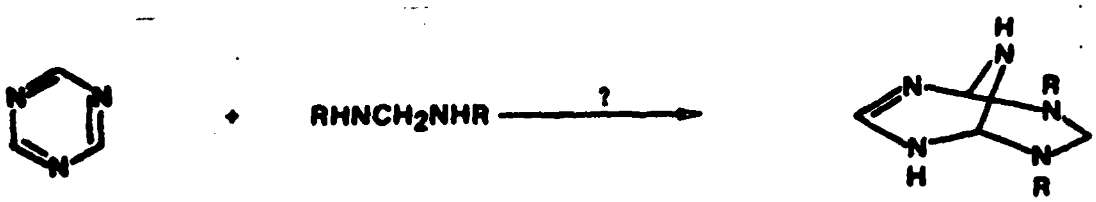
Unfortunately, methylenedinitramine and s-triazine are unreactive up to about 100° in either dimethylsulfoxide or pyridine as solvents. Reactions conducted at higher temperatures resulted in decompositions of the nitramine as judged by following the reactions by ^1H NMR spectroscopy. In addition, reactions of the triazine with both the mono- and disodium salts of methylenedinitramine were unsuccessful. Likewise, neither ethylenedinitramine nor methylenebisacetamide appear to react with s-triazine before decomposition occurs.



In contrast to the above results with weakly nucleophilic reagents, amines react readily[8] with s-triazine at room temperature although ethylenediamine does not give the desired bicyclic product.[8]



An examination of the reaction of s-triazine with methylenediamine was therefore initiated.



R = H

Methylenediamine is known in the form of its salts with strong mineral acids.[11] However, the free base generated from these salts in aqueous solution is unstable. Furthermore, s-triazine readily reacts with water. Therefore, a method of generating methylenediamine under non-aqueous conditions was sought.

---

11. P. Knudsen, Chem. Ber., 47, 2698 (1914). R. Ohme and E. Schmity, Chem. Ber., 97, 297 (1964).

Carbamates are reportedly cleaved readily to the free amine under neutral conditions with trimethylsilyliodide.[12] However, application of this reaction to methylenebisurethane 11[13] proved unsatisfactory for the preparation of the free diamine due to the difficulty in separating the products.

$$\underset{\underline{11}}{H_3COOCHNCH_2NHCOOCH_3} \xrightarrow[(CH_3)_3SiI]{?} H_2NCH_2NH_2$$

An alternate more successful approach involves catalytic hydrogenolysis of methylenebisbenzylcarbamate 12.[14]

$$\underset{\underline{12}}{\phi CH_2OOCHNCH_2NHCOOCH_2\phi} \xrightarrow[H_2]{} H_2NCH_2NH_2$$

Thus hydrogenation of a tetrahydrofuran solution of 12 over 10% palladium on carbon at 40 psi and room temperature leads to methylenediamine as judged by subsequent conversion to the known methylenebisacetamide with acetic anhydride. Attempted isolation of the bisamine as well as an examination of its reaction with s-triazine are underway.

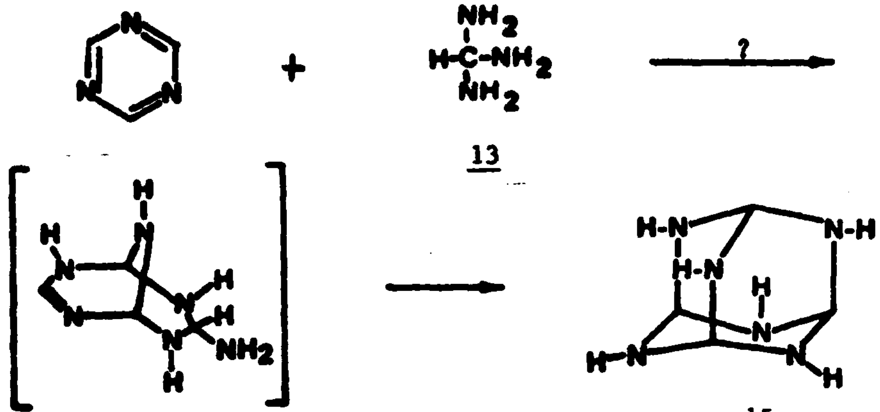
---

12. M. Jung and M. Lyster, Chem. Commun., 315 (1978). R. Lott, V. Chaukan, and C. Stammer, Ibid, 495 (1979).

13. M. Conrad and K. Hock, Chem. Ber., 36, 2206 (1903).

14. Prepared from benzylcarbamate and paraformaldehyde in a melt at 100° m.p. 148-149° (from acetonitrile)

We have undertaken the synthesis of the unknown trisaminomethane 13 in order to examine its reaction with s-triazine as a route to hexaazaadamantane.



A few substituted trisaminomethanes have been reported.[15] In the presence of excess acid, the compounds tend to lose one amine group with the formation of formamidines. This fact precludes the preparation of 13 via acid hydrolysis of tris(formylamino)methane[16] analagous to the preparation of diaminomethane salts from bis(formylamino)methane.[11] We therefore examined the previously mentioned trimethylsilyliodide cleavage of carbamates as a route to 13.

Reaction of tris(carboethoxyamino)methane 14[17] with the silyliodide in refluxing chloroform lead to the formation of formamidine (isolated as the hydrochloride) perhaps due to the temperature involved.

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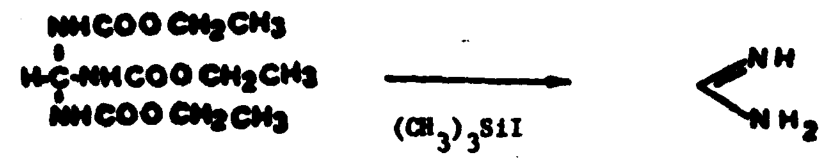
15. T. J. Atkins, J. Amer. Chem. Soc., 102, 6364 (1980). J. Erhardt, E. Grover, and J. W. Vest, J. Amer. Chem. Soc., 102, 6365 (1980) and references therein.

16. H. Bredereck, G. Gompper, H. Rempfer, K. Klem, and K. Keck, Chem. Ber., 92, 329 (1959).

17. V. Grakauskas, J. Org. Chem., 36, 3251 (1971).



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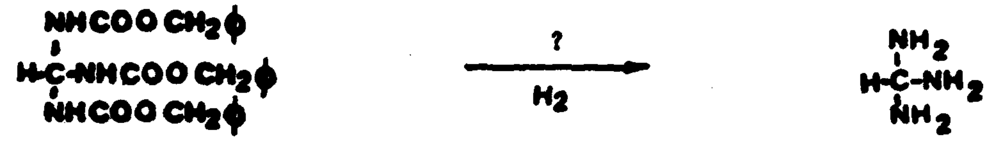
Since benzyl carbamates are reported to be cleaved by trimethylsilyliodide much more rapidly than alkyl carbamates[12], the tris(carbobenzyloxyamino) methane 15 was prepared[18] and its reaction with trimethylsilyliodide at room temperature was examined. However, to date we have been unable to confirm the success of this reaction.



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In view of our earlier success in hydrogenolysis of benzylcarbamates in the preparation of diaminomethane, we intend to apply this methodology to 15 in the near future.

The reaction of nitroguanidine with s-triazine in dimethylforamide or dimethysulfoxide at 150° leads to nitraminotriazine 16 and not the desired bicyclic system 17.[19] Using ^{1}H NMR, we have so far been unable to determine whether or not 17 is an intermediate in the formation of 16.

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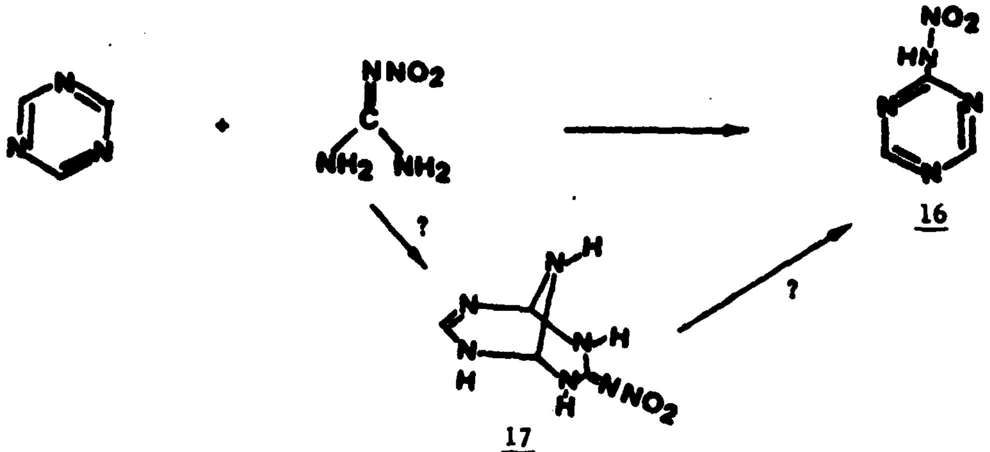
18. Prepared by the method of Grakauskas[17] using benzyl carbamate in place of ethycarbamate. m. p. 209-210° (from acetonitrile).

19. An analogous result is obtained with guanidine.[8]



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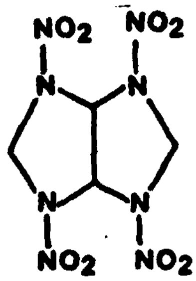
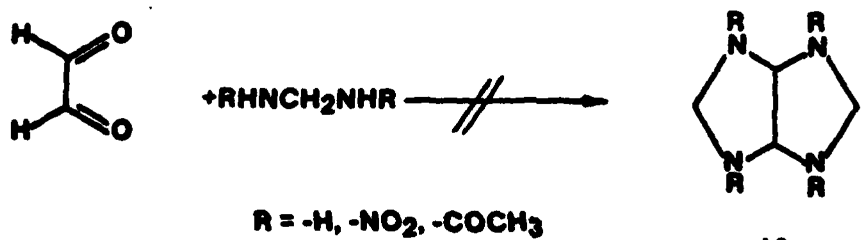
17

Compound II, N^1, N^2, N^3, N^4-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octane ("bicyclic HMX").



A number of attempts were made to construct bicyclic HMX or an appropriately substituted precursor via several cyclization routes.



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However, to date, we have been unsuccessful in obtaining the desired tetra-azabicyclooctane ring system 18 from these experiments.

Particularly frustrating has been the failure of tetranitraminoethane[20] to cyclize to II with formaldehyde.

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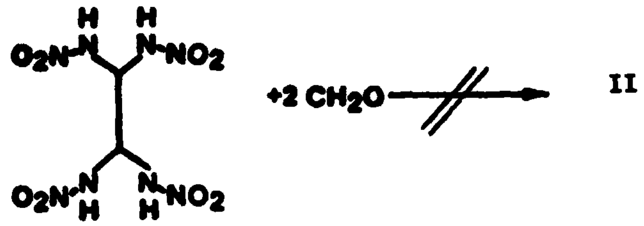
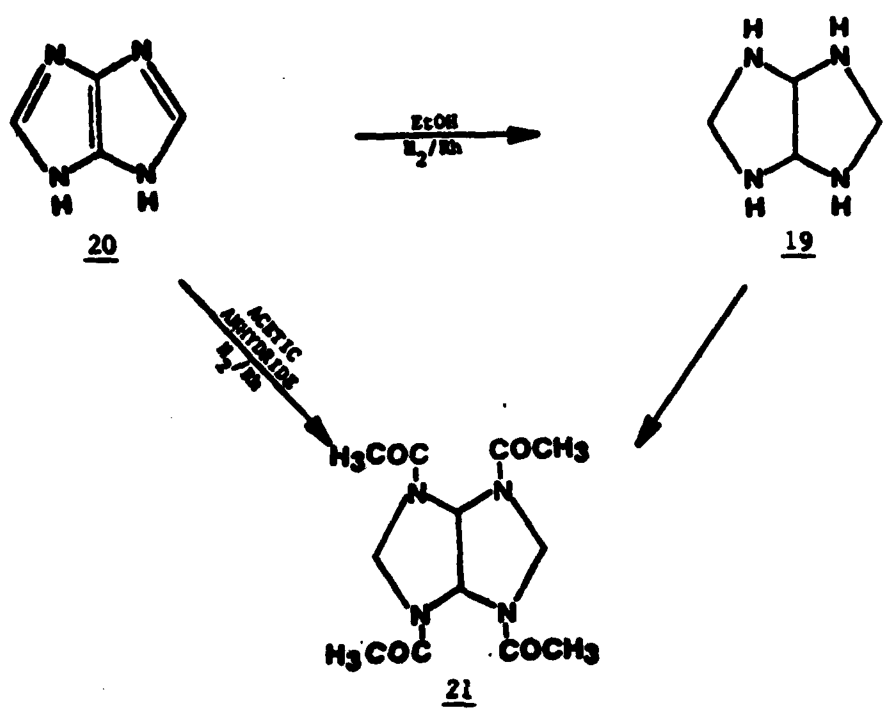
20. P. Zhongii and W. Daosheng, Acta Armamentaii, 3 (3), 23 (1980).



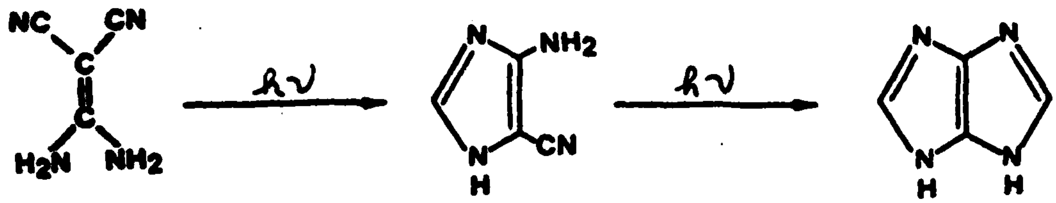
Attention was then directed toward the preparation of the desired aza-bicycloactane ring system 19 from the known[21] imidazo[4,5-d]imidazole 20.



21. J. P. Ferris and F. Antonucci, J. Amer. Chem. Soc., 96, 2010 (1974).

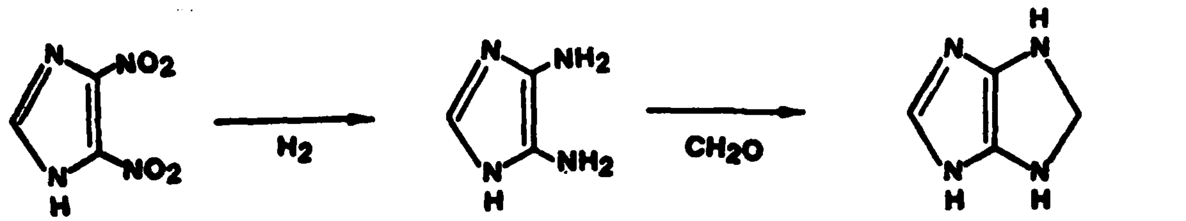
Catalytic reduction of 20 over rhodium[22] is expected to lead to the tetraazabicyclooctane 19. Nitration or nitrosation of 19 followed by oxidation should lead to II. Alternately, nitrolysis of 21 obtained either directly from 20 or via 19 also should lead to the desired oxidizer II.

Initial attempts to prepare 20 via the reported[21] photochemical cyclization met with some difficulty. In our hands, irradiation of 22 has lead only to intermediate imidazole 23, with none of the desired bicyclic 20 yet detected.



22 23 20

In another approach to compound 20 we have examined routes to the synthesis of the unknown 4,5-diamino-imidazole 24. It was hoped that cyclization reactions of 24 would lead to 20 or partially hydrogenated derivatives (e.g., 25).



26 24 25

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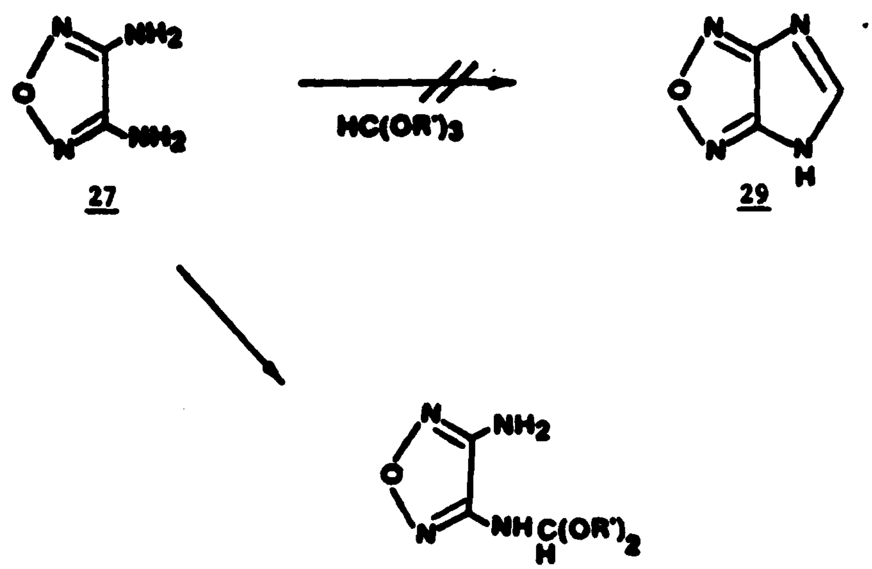
22. P. N. Rylander, "Catalytic Hydrogenation in Organic Synthesis," Academic Press, New York, 1979, Chap. 11 and 12.

However, to date, all attempts to hydrogenate the known[23] 4,5-dinitroimidazole 26 have lead to dark reaction mixtures from which the desired diamine 24 has yet to be isolated.

For this reason an alternate route to diamine 24 was devised.



27 29 28

Condensation of diaminofurazan[24] 27 with trimethyl orthoformate gave the uncyclized adduct 28 and not the desired bicyclic system 29. The use of higher boiling orthoformates to force the reaction will be attempted.

23. S. Novikov, L. Khmel'nitskii, O. Lebedev, V. Sevast'yanova, and L. Epashina, Khim. Geter. Soed., 6, 503 (1970).

24. M. Coburn, J. Het. Chem., 5, 83 (1968).